

Recent Advances in *In Situ* Water Quality Monitoring: Development of a Hexavalent Chromium Monitor

Joseph H. Aldstadt, Melissa A. Singer Pressman
University of Wisconsin-Milwaukee, WI

Goal and Scope. The cycles of many chemical species in natural waters are characterized by large changes in concentration over time. Daily variability can be driven by photosynthesis, respiration, and changes in the water column that are due to wave action and solar heating. Variations can occur seasonally as a result of changes in light, temperature, vertical mixing rates, etc. Other changes occur episodically, such as storms and algal blooms. These changes can only be accurately interpreted by the use of well-resolved time series measurements of chemical concentration. Conventional technology permits measurements only when ships are 'on station' — clearly there are not enough resources to provide the required resolution. In this presentation, following an overview of *in situ* measurement science, research in our laboratory to develop an *in situ* monitor for chromium speciation will be described.

Methods. The goal of our research is to develop and validate new methods for the chemical speciation of chromium in the environment. Specific objectives are: (i) design, assemble, and develop a novel *in situ* monitor for chromium speciation; (ii) use the monitor to study the dynamics of chromium in a representative high-energy surface water environment; and (iii) develop new laboratory-based methods that have high selectivity for chromium speciation to support the field studies.

Results and Conclusions. In this presentation, the design and testing of an *in situ* instrument for the chemical speciation of dissolved chromium at sub-mg/L levels in surface waters will be described. The proposed design couples membrane pre-concentration, trivalent-hexavalent speciation, Cr-1,5-diphenylcarbazide (DPC) complexation chemistry, and spectrophotometric detection in a microscale CFA manifold. A common problem encountered with the use of *in situ* monitors is the introduction of particulate matter into the system and the subsequent formation of organic layers on instrumental surfaces. A microporous membrane-based sample introduction method that minimizes this problem will be described. The detection approach, based on the spectrophotometric determination of hexavalent chromium as its DPC complex using a light-emitting diode visible source and photodiode detector, will be described also.

Recommendations and Outlook. The current methods for measuring chromium in surface waters have limitations because they are based on laboratory determination of the chromium species. For this reason, the high temporal resolution that is a prerequisite for a realistic understanding of the dynamics of chromium distribution and abundance in the environment is unattainable. That is, laboratory experiments provide a limited number of data points — samples cannot be practically collected and analyzed on a frequent basis (e.g., hourly). Since samples must be collected at the sampling site and then transported to a lab to determine the chromium content, contamination may easily be introduced. Furthermore, the lag time from sample collection to quantification can be significant, thus compounding the contamination probability as well as creating delays in providing information. These issues can lead to inaccurate models of chromium distribution and abundance for dynamic systems.